Performance Assessment of Innovative Constructed Wetland-Microbial Fuel Cell for Electricity Production

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Abstract
The objective of the present work is to decide whether a horizontal subsurface flow constructed wetland treating wastewater could function parallelly as a microbial fuel cell (MFC). Specifically, and as the main variable under study, different organic loading rates were used, and the response of the system was examined. The assembly consisted of a synthetic domestic wastewater-feeding system and a pilot-scale constructed wetland for wastewater treatment, which also included coupled devices necessary to function as an MFC. The wetland operated under continuous operation for 180 d, treating three types of synthetic wastewater with increasing organic loading rates: 13.9 g COD m⁻² d⁻¹, 31.1 g COD m⁻² d⁻¹, and 61.1 g COD m⁻² d⁻¹. The COD removal efficiencies and the cell voltage generation were continuously observed. The wetland worked concurrently as an MFC generating electric power. Under low organic loading rates, the wastewater organic matter was completely oxidised in the lower anaerobic compartment, and there were slight aerobic conditions in the upper cathodic compartment, thus producing an electrical current. Under high organic loading rates, the organic matter could not be completely oxidised in the anodic compartment and flowed to the cathodic one, which entered into anaerobic conditions and caused the MFC to become nonfunctional. The system established in this work offered similar cell voltage, power density, and current density values compared with the ones obtained in previous studies using photosynthetic MFCs, sediment-type MFCs, and plant-type MFCs. The light/darkness changes caused voltage fluctuations due to the photosynthetic activity of the macrophytes used (Phragmites australis), which affected the conditions in the cathodic compartment.

Keywords: Constructed wetland, Microbial fuel cell, Wastewater, Organic loading, Cell voltage

1. INTRODUCTION
Bioelectrochemical wastewater treatment has recently emerged as an auspicious technology that can be used to solve an environmental problem while helping to produce electricity from organic waste materials. Bioelectrochemical wastewater treatment is based on the fundamentals of Microbial Fuel Cells (MFCs).

MFCs use electrochemically active microorganisms that are adept of oxidising organic matter to generate electrons, protons, and other metabolic products. They produce extracellular electron transfer to an electrode (anode) while they are oxidising and removing the organic pollutants in wastewater. Via an electrical circuit, the electrons are conveyed to a cathode where they are consumed for oxygen reduction. The cathodic reaction can happen either through direct chemical catalysis or through biocatalysis in the case of a microbial biocathode. Due to this electrical connection, the electrode reactions can occur, and the electrons can flow from the anode to the cathode, permitting electrical current to flow (Rozendal et al., 2008).

The organic matter is oxidized in the anode (electrons are removed). The electrons created by the microorganisms are transported to the anode by electron shuttles, direct membrane-associated electron transfer, nanowires, etc. In most of the MFC, the electrons that arrive to the cathode combine with protons, which diffuse from the anodic compartment through a membrane, and with oxygen to produce water. It is not requisite to place the cathode in water or in a separate chamber when using oxygen at the cathode because the cathode can be designed for direct contact with air (Logan et al., 2006).
Different natural processes have been recently used as the base of the design of MFCs, leading to different configurations. The goal is always to reap energy contained in natural resources, such as the chemical energy of organic matter or solar power. There are different approaches that assimilate photosynthesis with MFC. When sunlight is converted into electricity within the metabolic reaction scheme of an MFC, the system is described as a photosynthetic MFC, and several configurations are possible (Rosenbaum et al., 2010). For example, it is possible to pair photosynthetic bioreactors using microalgae in the cathode with anaerobic oxidation of organic substrates in the anode produced by photosynthesis (Strik et al., 2008a) or contained in a wastewater flow (Lobato et al., 2013). Another configuration is the plant-MFC (De Schampelaire et al., 2008a; Strik et al., 2008b). The plant-MFC assimilates the roots of a living plant into the anode compartment of an MFC. The principal idea is that plant rhizodeposits will be consumed as substrates by bacteria in the MFC. Carbon dioxide is fixed from the atmosphere and released as root exudates by the plants. Root exudates are then utilised by microorganisms that return the carbon dioxide to the atmosphere. The microorganisms use the anode as an electron acceptor, and these electrons flow, due to the potential difference, to the cathode through an electrical circuit. To remain electroneutral, protons are conveyed through the membrane into the cathode where oxygen is reduced to form water.

Another method to reap energy from naturally occurring electropotential differences is to detect an anode into sediments in rivers or lakes, with immersion of a cathode in the overlying body of water. Such a set-up is called a sediment microbial fuel cell or benthic MFC (Reimers et al., 2006). The anode oxidises reduced compounds such as sulphides and fermentation products, whereas the cathode reduces oxygen near the water surface.

Bioelectrochemical wastewater treatment technologies based on MFC fundamentals are very novel technologies being developed. All the systems consisted of combined anaerobic/aerobic reactors in which different classical bioprocesses for nutrient and carbon elimination can occur. The assembly of an MFC in such collective processes is possible because of the presence of the two zones between which there is a difference of redox potentials. The number of articles published on this topic in recent years is very high. We cite here only some of them, such as recent reviews (Logan, 2012; Logan and Rabaey, 2012; Mook et al., 2013) and some studies on carbon and nitrogen removal (Virdis et al., 2008, 2010) and the application of MFCs to treat industrial wastewater (Velasquez-Orta et al., 2011).

One of the conventional low-cost technologies for wastewater treatment involves constructed wetlands (CWs). These systems entail wetlands that are isolated from the environment around them and receive wastewater. Depending on the type of CWs, they are designed by different elements including macrophyte plants, a porous solid bed, and a mixed population of microorganisms in the form of biofilms. Water purification is accomplished by a complex arrangement of natural physical, chemical, and biological phenomena (Zhi and Ji, 2012). Wastewater treatment wetlands have been used for decades, and there has been a considerable amount of research activity and literature published on this topic. One of the main types of CWs is the horizontal subsurface flow constructed wetland (HSSF-CW) in which water circulates through a porous bed of gravel on which macrophyte plants grow (Garci’a et al., 2010).

It is accepted that different microbiological mechanisms can take place in such systems, depending on the redox potential in the different zones of the porous gravel bed (Ojeda et al., 2008). Additionally, it is accepted that the upper parts of the wetland near the surface receive oxygen from the atmosphere, as do the inner zones closed to the rhizosphere because of the possible aeration potential of the plants, which COD Chemical Oxygen Demand (mg l\(^{-1}\)) are able to transfer oxygen to lower levels in the gravel bed (Garci’a et al., 2010). In contrast, deep zones in the wetland far from the influence of roots are mainly anaerobic zones. This situation illustrates conditions in which clear differences in redox potentials appear, and wastewater may be treated under different aerobic and anaerobic biological mechanisms. Because of this, according to the above description of the bioelectrochemical wastewater treatment fundamentals, in this work, the assumption that an MFC could be assembled to an HSSF-CW was considered as a starting point to achieve the objectives of treating wastewater and producing electricity from the oxidation of organic pollutants.

To date, no results similar to those described in this work were found in the literature, although there are some groups of researchers working on this topic. Only a few publications that used vertical flow subsurface systems (Yadav et al., 2012) or surface flow systems with floating...
macrophytes (Mohan et al., 2011; Chiranjeevi et al., 2013) were identified. In this context, the aim of the present work is to assess whether an HSSF-CWs could act simultaneously as an MFC. The authors used their previous experience in electrochemical engineering and in wastewater treatment involving biological processes using HSSF-CWs. Different organic loading rates were used, and the response of the system was monitored.

2. MATERIALS AND METHODS

2.1. Constructed wetland microcosm and microbial fuel

The experimental installation used was situated in a greenhouse next to the Department of Civil and Environmental Engineering, Aligarh Muslim University, Aligarh (India). The installation consisted of a synthetic domestic wastewater-feeding system and a pilot-scale HSSF-CWs for wastewater treatment modified to function as an MFC (Fig. 1).

The feeding system consisted of a 150 l agitated wastewater tank with temperature monitoring and a peristaltic pump that continuously fed the wetland. The wetland consisted of a 1.15m * 0.47m plastic channel with a bed depth of 0.50 m and a longitudinal slope of 1%. The wetland was filled with gravel with an average particulate diameter of 9 mm, apart from the left and right five-centimetre vertical layers, for which the average particulate diameter was 15 mm to improve the distribution of wastewater in the wetland. The bed porosity was 0.4. Sampling points were placed along the wetland at ¼, ½, and 3/4 of the total length. They consisted of vertical plastic tubes (3 cm diameter, and 10 cm length) perforated with several small holes (0.5 cm diameter) at different positions. The tubes were put in the wetlands before filling it with gravel. They made it possible to introduce temperature, dissolved oxygen, or redox probes. Phragmites australis (Reed) bought in a commercial greenhouse was planted in the wetland in autumn 2011 (20 plants m$^{-2}$).

An arrangement to transform the HSSF-CWs into an MFC was included during the wetland construction. A horizontal, rectangular (0.70 m * 0.15 m and 0.03 m thickness) graphite anode was located in the gravel bed, 12 cm above the bottom of the wetland, and an identical graphite cathode was also located 12 cm below the wetland surface. Both electrodes were in the subsurface of the water flow. The distance between electrodes was 25 cm. Insulated copper wires were used to connect both the electrodes, including a 120 U resistor between them.

A 0.02 m thickness layer of calcium bentonite (Bentonil A, from Su’d-Chemie) was placed in the middle depth of the gravel bed to separate the anode and cathode compartments and limit the growth of roots only to the upper area in which the cathode was located. The wastewater flow entered the system at the bottom anode compartment, passed through the compartment, and left through the opposite end. Subsequently, the wastewater was pumped to the cathodic compartment, passed through it via horizontal subsurface flow, and finally left the wetland.

2.2. Synthetic wastewater

Synthetic wastewater was always used in order to have control of the wastewater characteristics. Domestic, physically...
Table 1 - Composition (mg L\(^{-1}\)) of the three synthetic wastewaters used.

<table>
<thead>
<tr>
<th>Component</th>
<th>Wastewater 1</th>
<th>Wastewater 2</th>
<th>Wastewater 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>160.0</td>
<td>320.0</td>
<td>640.0</td>
</tr>
<tr>
<td>CH(_3)COONa.3H(_2)O</td>
<td>160.0</td>
<td>320.0</td>
<td>640.0</td>
</tr>
<tr>
<td>NaHCO(_3)</td>
<td>111.0</td>
<td>222.0</td>
<td>444.0</td>
</tr>
<tr>
<td>K(_2)HPO(_4)</td>
<td>44.5</td>
<td>89.0</td>
<td>178.0</td>
</tr>
<tr>
<td>MgCl(_2).6H(_2)O</td>
<td>37.1</td>
<td>74.2</td>
<td>148.4</td>
</tr>
<tr>
<td>CaCl(_2).2H(_2)O</td>
<td>30.1</td>
<td>60.2</td>
<td>120.4</td>
</tr>
<tr>
<td>(NH(_4))(_2)SO(_4)</td>
<td>111.9</td>
<td>223.8</td>
<td>447.6</td>
</tr>
<tr>
<td>(NH(_4))(_2)Fe(SO(_4))(_2).6H(_2)O</td>
<td>84.2</td>
<td>168.4</td>
<td>336.8</td>
</tr>
</tbody>
</table>

Pre-treated wastewater was simulated, using concentrated substrates that were later diluted with tap water in the feeding system. Three types of synthetic wastewater were tested to investigate the effect of providing different organic loading rates to the wetland. Table 1 shows the composition and parameters of the different types of wastewater used.

2.3. Experimental start-up and continuous operation

The experimental pilot plant was started by feeding wastewater 1 and seeding microorganisms by adding a small amount of biological sludge from the anodic compartment of a laboratory-scale MFC treating similar wastewater (González del Campo et al., 2013). The seed was added to the lower compartment of the wetland.

The wetland worked under a continuous operation mode, and the organic loading rate was the only variable under study. Three types of wastewater were used (Table 1), with their respective organic loadings, during three consecutive periods. Period I (during February to May 2012, 110 days) used an average COD influent of 250 mg L\(^{-1}\), and the organic loading rate was 13.9 g COD m\(^{-2}\) d\(^{-1}\). Period II, during May-July 2012 (day 110 to day 160) used 560 mg COD L\(^{-1}\) and 31.1 g COD m\(^{-2}\) d\(^{-1}\). Finally, period III (July-August 2012, day 160 to day 180) used 1100 mg COD L\(^{-1}\) and 61.1 g COD m\(^{-2}\) d\(^{-1}\). The first period lasted longer because it included the start-up process. A constant wastewater flow of 30 L d\(^{-1}\) was used to maintain a hydraulic residence time of 3.2 days. The wastewater pH was always maintained at approximately 7.4 by means of the buffer capacity of the synthetic medium. Despite the air-conditioning system available, temperature fluctuations of the ambient air in the greenhouse ranged between 18 and 31°C, depending on the external weather. It caused wastewater temperature fluctuations between 20 and 26 °C.

2.4. Sampling, analysis, and electrochemical monitoring

The whole system was monitored every three days. The influent flow was measured. Samples of the influent and effluent water flow were taken, and soluble COD was analysed in the laboratory according to the standard methods (A.P.H.A., 1998). The water temperature, pH, dissolved oxygen level (DO), and redox potential (ORP) in the cathodic compartment were monitored in situ using the sampling points. The pH and ORP were measured by a pH-meter (PCE-228M). DO was measured using a YSI 5000 dissolved oxygen probe. During regular process, the anode and the cathode were connected by means of wires and the resistance. The potentials between the edges of this resistance were incessantly supervised. A digital multimeter was connected to the system to continuously observe the value of the cell potential.

2.5. Electrochemical characterisation

To symbolize the electrochemical behaviour and performance of the HSSF-CWs, a polarisation curves were documented, and the equivalent power density curve was determined. The polarisation curves from the MFC test provide remarkable evidence about the functioning conditions of the MFC, in particular, about the actual competencies of the MFC. These curves make it possible to distinguish three important parameters: the open circuit voltage (OCV) or the maximum allowable MFC voltage (for a zero current), the maximum intensity reachable (for a zero potential), and the maximum feasible power density. In addition, the shape of the curve gives information about the restrictive stage that controls the performance of the cell. In this work, the polarisation curves were
determined by connecting different resistors, between 220.000 and 47 Ohms, to the MFC and measuring the resulting steadystate voltage.

3. RESULTS AND DISCUSSION

We considered a number of assumptions, which led to the construction and operation of the wetland in the manner described in Section 2. As a result, an experimental wetland ecosystem was developed for scientific research, including the usual elements in HSSF-CWs: the gravel bed, emergent plants, microorganisms and wastewater. The gravel bed used pretends to be inert material, with an adequate particle size to allow the subsurface flow; the plants used (Phragmites australis) are probably the most usual in this kind of experimental wetlands; the inoculum comes from an experimental MFC (this is an important difference) although the microbial culture is expected to change during the continuous process depending on the experimental conditions; finally, a synthetic wastewater has been prepared according to the large amount of previous experiences regarding the use of HSSF-CWs for wastewater treatment. The main differences in the artificial environment, compared to the usual HSSF-CWs, are the electrodes, the bentonite layer and the consecutive flow between the two compartments.

In this constructed wetland is perfectly acceptable that the lower compartment was operated under anaerobic conditions. The oxidation of organic matter (that is, the electron removal) was also expected to occur. Furthermore, the upper part of the wetland is in contact with the atmosphere and is further supplied by the rhizosphere, which should transfer oxygen from the air. Therefore, a potential difference should be generated between both zones. If an electrical current could be generated between the electrodes, the transport of H\textsuperscript{+} ions would be achieved through the water flow between both compartments. The intermediate layer of bentonite, even though it is also permeable to the transport of H\textsuperscript{+}, primarily serves to separate the aerobic and anaerobic zones.

Fig. 2 shows the dissolved oxygen and redox potential profiles in the upper cathodic compartment during the whole experimental period (periods I, II, and III, using increasing organic loads). The data plotted in Fig. 2 are mean values of the ones obtained at the same time in the different sampling points (Fig. 1). Approximately constant levels of dissolved oxygen (2 mg l\textsuperscript{-1}) and redox potential (-30 mV) could be observed during period I. The dissolved oxygen level in this type of wetlands is usually very low (García et al., 2010); thus, a 2 mg l\textsuperscript{-1} concentration could be considered a relatively high level. The values of both parameters dropped during period II. Finally, an abrupt decrease was observed during period III, and the dissolved oxygen practically disappeared. The pH value remained approximately constant at 7.4 during the whole experimental period.

Fig. 3 shows the wetland influent and effluent COD concentrations and the measured cell voltages during the whole experimental period. Both Figs. 2 and 3 provide insight into how the system works. After seeding the system with microorganisms from an MFC, the start-up stage lasted for...
Fig. 3 - Influent and effluent COD and cell voltage measurements during the whole experimental period.

approximately one month. COD and voltage measurements started at day 30. It can be observed in Fig. 3 that the effluent COD value is very low starting at day 50 and that COD is completely removed from day 65 to the end of period I. At the same time, low cell voltage values were detected starting at day 50, and they clearly augmented between days 60-90. Finally, they steadied at approximately 240 mV. Considering the fact that the dissolved oxygen level could be considered to be relatively high in period I, it can be presumed that the initial postulation of the work was satisfied, that is, that the wastewater organic matter was completely oxidised in the lower wetland compartment and that the upper wetland zone worked under slightly aerobic conditions, causing electric current to be produced.

Several factors could stimulate the electricity generation in this system. One of them is the necessary aerobic environment in the upper wetland zone, which in part depends on the potential aeration of the plants. In general, the aeration potential of macrophytes is rather less compared with the conventional aeration systems in wastewater treatment plants. Specifically, the aeration potential of Phragmites australis in such wetlands has been measured in previous research, and different values were obtained. Armstrong et al. (1990) reported oxygen release values of 5-12 gO₂ m⁻² d⁻¹, and Gries and Garbe (1989) reported values of 1.5-3 gO₂ m⁻² d⁻¹. It is significant to notice that roots not only transfer oxygen but also produce organic matter as rhizodeposits or exudates (Tanner et al., 1998) that will consume part of the dissolved oxygen. Specifically, the amounts of dissolved organic carbon released from roots of Phragmites australis has been recently measured by Zhai et al. (2013). The fact that, despite this situation, the dissolved oxygen values detected were approximately 2 mg l⁻¹ would specify that no organic matter from the wastewater reached the upper zone. Thus, the wastewater was nearly completely oxidised in the lower anaerobic zone. Otherwise, the oxygen levels could not be preserved at this level. The capacity of roots to exudate organic matter as rhizodeposits was considered by previous studies, which reflected that roots should be located around the anode in other types of MFCs (Chiranjeevi et al., 2012; De Schamphelaire et al., 2008a; He et al., 2009; Strik et al., 2008b). In contrast, the present paper aims to give importance to the oxygenation capacity of the roots, and therefore, they were placed in the cathodic zone.

The influent COD and organic loadings were augmented during periods II and III. Fig. 3 shows that COD removal efficiency during period II reached values between approximately 90% and 95%. During days 110-130, the cell voltage remained at the values perceived at the end of period I, and the voltage clearly amplified after day 130. Important cell voltage fluxes were observed between days 130 and 160, with an approximate average value of 700 mV. The maximum value was 1161 mV.
Voltage fluctuations would seem because is very difficult to keep absolutely constant values of the experimental conditions in such a natural system. Voltage fluctuations were larger in period II, because they resembled to an average value of voltage higher than in the period I.

The deletion efficiency of COD during period III was also extraordinary (between 80% and 85%), but the effluent COD concentration sometimes surpassed the level of 200 mg l$^{-1}$, and

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average voltage (approximately 700 mV)</th>
<th>Maximum voltage (1161 mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulombic efficiency (%)</td>
<td>0.27</td>
<td>0.45</td>
</tr>
<tr>
<td>Power density (mW m$^{-2}$)</td>
<td>15.6</td>
<td>43.0</td>
</tr>
<tr>
<td>Current Density (mA m$^{-2}$)</td>
<td>22.3</td>
<td>37.1</td>
</tr>
</tbody>
</table>

The cell voltage considerably reduced. Furthermore, Fig. 2 shows a clear decrease of the redox potential and the fading of the dissolved oxygen in the upper wetland zone. This situation would specify that the organic matter was not completely oxidised in the anodic zone and that it reached the upper zone, generating an oxygen demand greater than the oxygenation potential in this zone and thus motivating the consumption of the dissolved oxygen. As a result, the upper zone transformed to anaerobic conditions, the COD was not completely detached, and it is expected that the potential difference between the two zones of the wetland was greatly reduced.

Different performance parameters have been calculated from the experimental results and are included in Table 2. These parameters deliver evidence about the electric power generation ability of the wetland. Calculations have been performed according to Logan et al. (2006) using the experimental results from operation period II.

Table 2 shows very low coulombic efficiencies compared with several previously reported values obtained in common biological wastewater treatment systems with an MFC assembly. He et al. (2005) reported coulombic efficiencies between approximately 1% and 7%, and Virdis et al. (2008) reported values between 15% and 45%. Regarding the power efficiency of the system, it would be reduced because the use of some devices like pumps, although it must be noted that this is an experimental prototype which must use some power consuming devices in order to maintain experimental conditions, but they are not used in full scale systems.

In contrast, the cell voltage, power density, and current density values obtained in this work are similar to the ones obtained in previous works using photosynthetic MFCs, sediment-type MFCs, and plant-type MFCs. Zou et al. (2009) reported power density values of approximately 1 mW m$^{-2}$, and current densities up to 30 mA m$^{-2}$ using a photosynthetic MFC. Strik et al. (2008b) reported 67 mW m$^{-2}$ as maximum value, whereas De Schamphelaire et al. (2008a) reported values between 10 and 20 mW m$^{-2}$, with both works using plant-type MFC. Regarding the sediment-type MFC, Logan et al. (2006) showed that this type of MFC can produce a power density of up to 28 mW m$^{-2}$, and De Schamphelaire et al. (2008b) indicated that the average power values are on the order of 10e20 mW m$^{-2}$. The few known systems based on constructed wetlands reported 35 mW m$^{-2}$ as the maximum power density value (Yadav, 2010), 16 mW m$^{-2}$ as the maximum power density value and current density values up to 70 mA m$^{-2}$ (Yadav et al., 2012), and power density values
between 17 and 80 mW m\(^{-2}\) (Mohan et al., 2011). Based on these results, HSSF-CWs coupled with MFC would harvest similar electric power to the one produced by conventional sediment-type MFC and plant-type MFC. The main advantage of HSSF-CWs would be that wastewater pollutants removal could be concurrently accomplished. In contrast, the main drawback would be the need to shape and operate the wetland, although construction and operation costs are very low. Fig. 4 shows the day/night cycles, the profiles of the ambient temperature in the greenhouse, and the cell voltage measurements during a 4 day period in July 2012 (period II).

The day/night temperature variations were between approximately 18 and 31ºC. These oscillations seemed to have a direct influence on the cyclic temperature changes, and the light/darkness changes had a direct effect on the voltage variations, except for a short period at 40 h, where there was a slight delay in the voltage daily cyclic distinction. Because of this possible relationship, the voltage data plotted in Fig. 3 were always measured at the same each day (between approximately 10:00 and 13:00).

According to González del Campo et al. (2013), there is little information available about the influence of temperature on the performance of MFC systems treating wastewater. They resolved that a rise in temperature initiated a rise in the cell intensity, most likely due to the greater microbial activity. However, in the present work, it is presumed that the light/darkness change is the main factor that caused the voltage instabilities, and this could be related to the photosynthetic activity of the macrophytes.

Sunlight origins photosynthetic activity in plants and thus reasons changes in the operating conditions in the cathodic compartment because of the presence of the rhizosphere. Photosynthesis causes oxygen production through the plants roots, which would yield a redox potential increase and thus have a positive influence on the MFC performance. However, photosynthesis also causes organic matter generation (root exudates) in the cathodic compartment, which would have the contradictory result on the MFC performance. The results attained in the present work specify that sunlight caused a cell voltage increase, and so it is clear that the oxygen

![Fig. 5 - Polarisation curve obtained under stationary conditions at the end of period I.](image)
generation effect was more important than the exudate production. The cell voltage decreased at night. The same behaviour has been previously observed and explained by Zou et al. (2009) using a photosynthetic MFC.

There are also some research studies using plant-type MFCs or sediments-type MFCs in which the light/darkness changes also affected cell voltage variations, but in the opposite direction to those observed in the present work (Chiranjeevi et al., 2012; De Schamphelaire et al, 2008a; He et al., 2009; Strik et al., 2008b). The reason is that the rhizosphere in these works was located in the anode compartment, and thus the same phenomena (oxygen generation and organic exudate generation) had the opposite effect on the MFC performance compared with the present work.

The system was electrochemically categorized through a polarisation curve (see Fig. 5), which was obtained at the end of period I. As seen in the polarisation curve, the voltages output of the HSSF-CWs declined when diminishing the resistor loads following the typical trend (Logan et al., 2006). The shape of the curve obtained clearly showed the three major losses of the fuel cells.

The first losses (section A) were due to the activation losses, which could be elucidated because of the very poor reaction kinetics of the organic matter degradation in the anodic chamber. The total contribution of the activation losses in the HSSF-CW was approximately 75% of the losses (0.55 V).

The second voltage loss (section B) is due to ohmic loss. In this case, the ohmic loss was approximately 0.04 V, and the ohmic resistance of the system was approximately 120 Ω. Taking into account the electrode area, the Area-Specific Resistance was approximately 31.3 Ω.m². This value is very high, but it can be explained by the thickness of the electrode.

The last voltage loss (section C) is due to the concentration loss. This is due to the depletion of the substrates oxidised in the anodic chamber, in this case, the organic carbon source contained in the wastewater or the accumulation of protons in the nearby electrolyte. The voltage drop caused by the concentration loss was approximately 0.12 V.

From the polarisation curve, it was observed that under the stationary conditions in period I, the maximum voltage and current density reached were approximately 746 mV and 1.24 mA m⁻² respectively. The maximum power density reached was approximately 0.17 mW m⁻². This value was obtained at an optimal current density of approximately 1.12 mA m⁻² and at an optimal voltage of approximately 125 mV. These results indicate that the internal resistance of the HSSF-CW was approximately 120 Ω, which match with the resistance load connected during operation, suggesting that the bioelectrogenic operation has been acclimated to this load condition.

4. CONCLUSIONS
An HSSF-CWs treating domestic wastewater can act at the same time as an MFC generating electric power. Under low organic loading rates, the wastewater organic matter is completely oxidised in the lower anaerobic compartment, and there are slight aerobic conditions in the upper cathodic compartment, thus triggering an electrical current. Under high organic loading rates, the organic matter cannot be completely oxidised in the anodic compartment and flows to the cathodic one, which go in into anaerobic conditions, and the MFC stops working. The system developed in this work offered analogous cell voltage, power density, and current density values to the ones obtained in previous works using photosynthetic MFCs, sediment-type MFCs and plant-type MFCs. The light/darkness changes caused voltage fluctuations due to the photosynthetic activity of the macrophytes, which affected the conditions in the cathodic compartment.

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6. REFERENCES


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